Journal of Membrane Science 464 (2014) 86–99

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Integration of membrane technology in microalgae biorefineries

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ARTICLE INFO

Article history:
Received 20 November 2013
Received in revised form
2 April 2014
Accepted 5 April 2014
Available online 13 April 2014

Keywords:
Microalgae
Biorefinery
Membrane technology
Biodiesel
Review

ABSTRACT

The future of microalgae as a sustainable feedstock for biofuel and other products is still uncertain. Although productivity and environmental benefits surpass that of many other types of feedstock, the associated costs with production and downstream processing hinder this type of technology. The microalgae biorefinery approach addresses many of these issues in which upstream and downstream processes are important. Upstream technologies associated to nutrient recovery from waste effluents have been reviewed and discussed. Potentially, waste-derived nutrients will enable the formulation of optimal growth media from wastewater at lower costs. Microalgae dewatering is still seen as a major burden. A thorough review of the associated membrane processes in the literature has highlighted lack of consistency in terms of the influence of pore size and membrane materials. Moreover, only very few pilot-scale cost estimates could be found. The fractionation of microalgae products is perhaps the less developed area in the context of a microalgae biorefinery. Membrane filtration for the recovery of lipids, proteins and carbohydrates from microalgae is still an infant technology and major developments are expected to take place within the next few years. This review highlights the achievements, potential and future challenges of integrating membrane technology into microalgae-based biorefineries.

1. Introduction

Motivated by market demand for sustainable sources of fuel and energy, biofuels have become a priority for most governmental energy agendas. Nevertheless, in recent times the analysis of the environmental implications in terms of farmland loss and CO_2 emissions has changed our perception of crop-derived biofuels. This has led the EU to reduce the 10% target for renewable energy in the transport sector by 2020, down to 5% [1,2]. Moreover, in order to feed a growing population, farmland is continuously extending into tropical forest areas which threatens biodiversity and the global environment [3,4]. Seemingly, there are divided efforts between growing crops for fuel and energy or for human nutrition.

The need for alternative and sustainable sources of both food and energy has led microalgae to be regarded as a potentially viable feedstock [5–7]. Through a photosynthetic process, microalgae are able to uptake metals and nutrients like carbon (as CO_2), nitrogen (as NH_4^+/NH_3 and NO_3^-/NO_2^-) and phosphorous (as PO_4^{3-}) for their growth and transform these into valuable products such as proteins, carbohydrates, lipids and silica nanomaterials (in the case of diatoms). Whilst algal proteins and poly-unsaturated fatty acids (PUFAs) are driving the use of microalgae as feed and "foodstuff", the biofuel focus is uniquely related to the level of lipids which can be chemically transformed into biodiesel [8–10]. Other forms of fuel such as methane from the anaerobic digestion of algae biomass [11,12] and bioalcohol [13,14] have also been reported in the literature. Apart from fuel commodities, a handful of high-value products have been related to microalgae. These tend to be poly-unsaturated fatty acids (PUFA's) such as eicosapentaenoic acid (EPA) [15,16] and decosahexaenoic acid (DHA) [17], antioxidants such as astaxanthin [18], proteins [19,20], pigments such as chlorophyll and carotenoids [21] and a mixture of polysaccharides [22,23]. EPA and DHA are known to have a variety of health benefits such as hypotriglyceridemic and anti-inflammatory properties [24,25]. Astaxanthin is a potent antioxidant carotenoid also known for anti-inflammatory, antitumor and cardio-protective effects [26,27]. Due to their functionality, emulsifying and enzymatic properties, proteins are very useful in both the food and cosmetic industries [19,20,23]. Certain carotenoids such has beta-carotene, lycopene and astaxanthin are an important dietary source of vitamin A and used to treat certain skin diseases [28]. Chlorophyll is regarded as a colourant and functional ingredient for food processing [29] and also has known antioxidant properties [30,31]. Polysaccharides may represent both an additional ingredient in food processing and a carbohydrate source for bacteria and yeast [14]. The overall composition of algae can be simplistically divided in to three main biochemical groups: proteins, lipids and carbohydrates, although authors also

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http://dx.doi.org/10.1016/j.memsci.2014.04.010
0376-7388/

include ash and carotenoid content in their work [20,32,33]. Nonetheless, the biochemical composition is highly dependent on numerous environmental and nutritional factors within the growth strategy implemented. These include the composition and supply strategy of the growth media [34–36] and light intensity [37,38]. This variability of the biochemical composition may represent an added challenge for membrane filtration processing but most importantly allows a very flexible product-orientated feedstock.

Due to the photosynthetic ability to take up CO_2, metals and nutrients from waste effluents microalgae are also regarded as a bioremediation tool. On CO_2 sequestration, it has been reported that microalgae could capture 1.8 kg CO_2/kg biomass (absorbed via photosynthesis) [8,39] and have very high capability to remove nitrogen, phosphorous and sulphur compounds from wastewater [40,41]. Furthermore, cultivation technologies of microalgae biomass do not normally compete for arable land which would otherwise undermine the efforts to meet food demand [42,43]. As a result, microalgae appear to be a more socially and environmentally responsible source of biofuel and organic chemicals.

The importance of algae as a potentially viable feedstock has prompted the development of associated processing technologies which allow maximising product output and reduce costs. Across many industry sectors membrane technology has become a pivotal technology in meeting the demand for a wide range of commodities such as water, food, energy, speciality products and even in wastewater treatment [44–48]. Membrane separation is a process which selectively allows mass transfer of materials from one phase to another, usually driven by pressure, concentration, chemical or electrical potential gradient [49,50]. In simple terms, membranes are classified according to their pore size which range from micron pore size to angstroms, e.g. microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). These can also be distinguished according to the fabrication material (e.g. zeolite, organic and inorganic) and configuration (e.g. spiral-wound, fibres and tubular) [51]. One of the earliest studies of membrane phenomena dates back to the middle of the eighteenth century and referred to the selective passage of water using a pig's bladder [52]. Nevertheless, only in the 1960s, with the development of synthetic membranes by Loeb and Sourirajan [53], membranes were seen as a valuable technology for the process industries. Only 20 years later membranes were effectively being applied at industrial scale. Today, membranes are widely used throughout industry and have become the dominating technology in some cases [50]. Particularly for desalination, technologies such as reverse osmosis have overtaken thermal desalination in terms of metric tons of fresh water produced and account for around 60% of the worldwide production capacity [54,55]. Table 1 summarises some of the documented applications of membrane separation and the specific membrane types used. The rise of membrane technology is a consequence of their own merits over competing technology. Such advantages which account for this success include the ease of scaling up, chemical free separations, low operating and maintenance costs, compact and modular design, automated and continuous operation whilst allowing for highly selective separations [49–51,56,57]. In many cases, dewatering using membranes is preferable to thermal processes due to the reduced minimum work versus energy demand for a phase change.

One of the most recent challenges for membrane filtration is the integration into biorefineries. The biorefinery concept is often described as a facility which converts biomass and biomass wastes into valuable commodities such as fuel, solvents, plastics and added-value chemicals [112–114]. Seemingly, biorefineries represent an opportunity for membrane technology since many of the downstream processes can be realised using available membrane methods. Abels et al. [115] and He et al. [116] have thoroughly reviewed the membrane technologies associated to bioenergy and biorefining. When focused on the utilisation of lignocellulosic materials as a bio-

Table 1
Examples of the application of each type of membrane filtration in specific industry areas. MF – microfiltration, UF – ultrafiltration, NF – nanofiltration, RO – reverse osmosis, FO – forward osmosis, PV – pervaporation, ED – electrodialysis, and GS – gas-solid.

Applications	Membrane type	Reference
Food and biotechnology		
Cell harvesting, e.g. algae, bacteria and yeast	MF/UF	[58–61]
Juice, wine and beer clarification	MF/UF	[62–65]
Milk processing and fractionation	MF/UF	[66,67]
Recovery and fractionation of protein and peptides	MF/UF/ED	[68–73]
Sugar refining and clarification	MF/UF/NF/RO	[74–78]
Concentration of foodstuff and pharmaceuticals	NF/RO/FO	[79–84]
Energy, fuels and solvents		
Extraction and purification of bio-oils and biodiesel	MF/UF/NF	[85–89]
Recycling and purification of organic solvents	NF	[90–93]
Extraction and purification of alcohols	PV	[94,95]
Biogas processing and upgrading	GS	[96,97]
Environment and water treatment		
Wastewater remediation	UF/NF	[98–100]
Heavy metal removal/recovery	NF/ED	[101–103]
Desalination for fresh water supply	NF/RO/FO	[104–107]
Recovery of resources from wastewater	MF/UF/NF/RO	[108–111]

renewable feedstock, Abels et al. [115] reported the exploitation of membranes for the production of sugars, lactic acid, proteins, amminoacids, bio-ethanol, biodiesel, lignin and antibodies. In addition, a more extensive review by He et al. [116] also covered the application of membrane technology in biogas and hydrogen production, extraction of bio-oil, purification of biodiesel and bioethanol processing. Many of the opportunities and challenges for integrating membrane technology in biorefineries have been highlighted by these authors, however, the availability of feedstock and the market value of the products generated will drive the decision making process. Setting aside the environmental considerations, microalgae have a very favourable composition with only 4–10% ash matter [32,33] and low lignin present in the cell wall which contains poly-ionic saccharides [117]. Therefore at least 90% of the algae biomass could be processed for marketable products. Table 2 summarises the biochemical composition of different feedstocks used for fuel, energy, feed and food. Although the productivity of microalgae surpasses that of any other feedstock, the reported 100 ton/ha/year of microalgae is yet to be demonstrated at full scale. The world's largest microalgae production plant is 250 ha set up in a series of artificial ponds and is found in Hutt Lagoon, Australia. *Dunaliella saline* is cultivated for the extraction of beta-carotene. A few companies such as Cyanotech corp. (Hawaii, USA) and Nature Beta Technologies (Israel) supply a range of microalgae based products such as skin-scare and food supplements.

1.1. Key challenges for microalgae processing

As the research community attempts to unlock the potential of microalgae, many technical and non-technical challenges hinder the feasibility of this novel *green technology*. Commercially, microalgae struggle to become viable since microalgal economics are fundamentally based on the extraction of algal-oil [5,9]. Thus far, only a handful of technologies have been reported for the extraction of microalgae products. Moreover, these uniquely target on one product (typically lipids) and thus do not account for the viability and value of the remaining products in the biomass [16,138]. The prospects in marketing microalgae-based products seem to rely on the cost reduction of the inputs such as energy, water and nutrients but also in maximising the range of products. Only an integration of upstream and downstream processes will

allow maximising profits and reducing costs. One such concept is the biorefinery model. Greenwell et al. [6], amongst others, have introduced the concept of microalgae biorefineries highlighting the range of possible algae-derived products. Using waste streams as a source of nutrients, water and CO_2 this approach has little waste products and allows for the recovery of waste energy, nutrients and water purification [6]. The implementation of a biorefinery is hindered by numerous obstacles associated with energy costs and viability of the technologies. Mild extraction techniques are necessary in order to avoid compromising the integrity and extraction of the potential products. Moreover, the utilisation of waste sources requires the consideration of health and safety issues and low-cost processes which make the wastes amenable for biomass production and product marketing.

Little work has been published in relation to microalgae biorefineries and many authors have failed to highlight the advantages and drawbacks of the associated processing technologies. The use of supercritical CO_2 has been reported in relation to oil and pigment production in a biorefinery context, however, this technology is harsh and obliterates the remaining algal products [139]. Vanthoor-Koopmans et al. [10] have reported the use of surfactants for protein extraction whilst lipid extraction was proposed by ionic liquids coupled to chromatographic separations. Even though these are mild extraction methodologies, they represent a more complex approach and may also contaminate some of the products of interest [10]. Such publications have failed to acknowledge the scope of application of membrane technology but most importantly they have focused on typically harsh and energy intensive methodologies [140]. Fig. 1 illustrates the microalgae biorefinery concept which includes the exploitation of low cost inputs as nutrient sources, dewatering of microalgae and focuses on the downstream processes of multiple products. There are three key areas where membranes pose as a feasible technology: (1) upstream technologies for the extraction of nutrients, (2) cell harvesting and (3) downstream processing (DSP) to algal products. This review highlights the recent advances and applications of membrane operations in the context of microalgae biorefineries. We have also proposed membrane-based processes which assist towards the feasibility of the microalgae biorefinery. Although this review is limited to these three main areas, the authors acknowledge that water and flue gas treatment by membrane processes are also of interest. Nevertheless, such applications have already been comprehensively reviewed previously [141–144] and are excluded from this paper.

Table 2
Productivity and biochemical composition of different feedstocks used in renewable energy and biorefining.

Feedstock	Productivity (ton/ha/year)	Carbohydrates (%)	Proteins (%)	Oil content (%)	Energy (MJ/kg dry biomass)
Microalgae[a] [20,33,43,120–122]	60–100[b]	8–64	6–71	15–73	28[c]
Wood (pine) [123–125]	3	65[d]	1	None[e]	57
Oil palm (as fruit) [126–129]	20–25	13–35	3–10	25–73	40
Corn (as seed) [130–132]	13	70–75	8–11	3–18	20
Soybean (as seed) [130,133,134]	3	35	40	20	19
Sugar cane [135,136]	60	12–16	None	None	3[f]
Rapeseed (as seed) [127,134,137]	3	None	20	45	17

[a] Biochemical composition depends greatly on the species and cultivation strategy.
[b] Depending on the bioreactor design and production mode.
[c] Assuming 50% lipids.
[d] As cellulose and hemicellulose.
[e] Oil yields of up to 75% are possible by pyrolysis of wood chips [118,119].
[f] 1 t of sugar cane gives 0.15 t of dried bagasse with a gross calorific value of 19.25 MJ/kg bagasse.

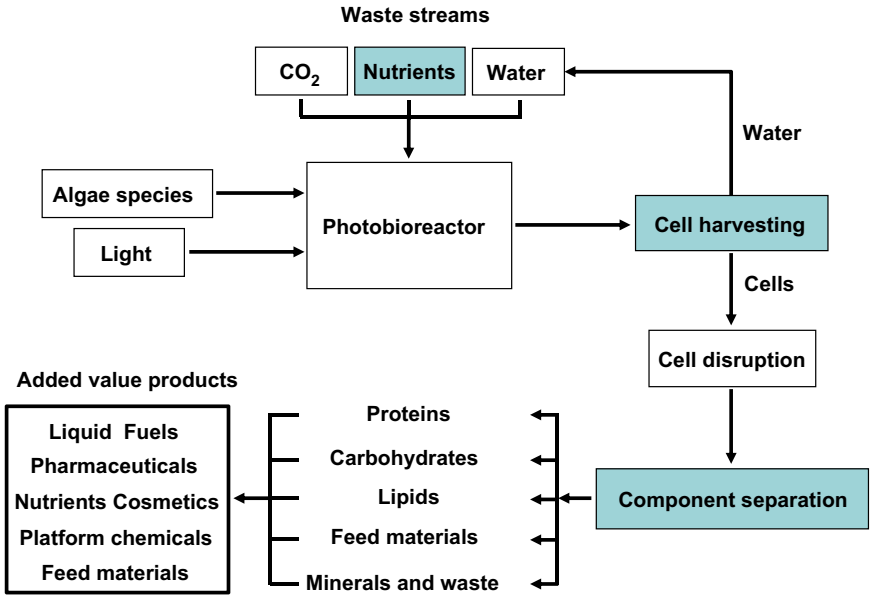

Fig. 1. Upstream and downstream requirements for a microalgae biorefinery. Integration of membrane technology is highlighted in blue. Adapted from [6].

2. Upstream processing

The cultivation of microalgae requires mainly nitrogen and phosphorous but also trace metals such as iron, manganese, copper, zinc and vitamins such as vitamin B1, vitamin H and vitamin B12 [145]. Estimations have shown that if microalgae were cultivated at 20% oil and around 50% protein, 0.2 kg nitrogen (0.26 kg NH_4^+ or 0.89 kg NO_3^-) and around 0.04–0.02 kg phosphorus are necessary per kg of microalgae [146]. Growth medium represents around 10% of the cultivation costs (0.44€/kg DW) whilst CO_2 accounts for another 6% of the final cost [147]. Life cycle analysis has concluded that the energy needed to create ammonium by the Haber-Bosh process accounts for 40% of all energy inputs for microalgae-based biofuel systems [148]. In addition, the use of phosphorus for microalgae cultivation directly competes with food supply. Indeed, phosphorus is an essential component to all living cells and has a crucial role in maintaining high crop yields which sustains the continuous growth of the global population. As peak phosphorous is expected to take place within the next decades the price of such a commodity is set to rise [149]. The production of such materials, especially nitrogen, is energy intensive with a large carbon footprint and an added cost in microalgae cultivation. Therefore, the future of microalgae systems requires adequate and sustainable source of nutrients. Reusing process water may recycle unspent nutrients, however, nutrient additions are still required and there is a high risk of undesired accumulation of some metals and contaminants such as poly-phenols, making this option very unattractive [150]. One of the most interesting options within a sustainable context is to use nutrient-rich wastewaters. As previously demonstrated, the integration of microalgae systems in wastewater treatment allows reducing nutrients, metals and some toxic organic compounds in wastewaters [151–153]. This synergy has been demonstrated for municipal [154], agricultural [155,156] and industrial wastewaters [157]. Nonetheless, the concentration of nutrients in wastewater is varied and in the case of phosphorus, typically bound as organic matter. In addition, wastewaters are complex, full of particulates and pathogens [158]. Therefore, although wastewaters are certainly a repository of materials, the recovery of these into sterile and particle free solutions is challenging. Table 3 highlights the varied composition of the different waste sources and the typically high solid content, especially for dairy manure and aquaculture farming.

The role of membrane technology in the recovery of vital microalgal nutrients from wastewaters is of significant importance. A comparative evaluation of the benefits and limitations of the available technologies is given in Table 4. Previous work [163] has already established the feasibility for the recovery of nutrients and metals from anaerobically digested dairy manure farm waste via microfiltration. Using diafiltration and acidification techniques, strategies have been developed which improve nutrient recovery yield and control the N:P ratio. The costs of this process using a ceramic microfilter were determined as 1.0€/m^3 leachate processed (logistical costs were not accounted for) [163]. With this approach, nutrients and metals were recovered in virtually sterile and particle free solutions.

Amongst others, microalgae growth media is commercially known as f/2 media and is typically related to that reported by Guillard [145]. Currently, f/2 media can be purchased from several suppliers at a varied range of prices (Table 5). Aside from the environmental importance of recovering nutrients from wastewater, the feasibility of the waste-derived nutrients depends on cost. The concentration of the major nutrients will determine the amount of wastewater needed per litre of microalgae culture. Table 5 demonstrates the nutrient cost of waste-derived nutrients against other commercially available products. With 200 mg NH_4–N/L present in the wastewater, cost with nutrients will be at least 10-fold less than the cheapest price found for f/2 microalgae growth media. Higher nutrient content will directly translate into lower nutrient cost for

Table 3
Composition of different waste sources based on nutrients and solids content.

Parameter	Waste source			
	Dairy manure[a]	Aquaculture [b,c]	Municipal[d]	Industrial [e,f]
TSS (mg/L)	888-39,300	16,580–31,010	n.d.	35
TN (mg/L)	225–2370	366–489	110	3
NH_4–N (mg/L)	178–1620	n.d.	92	2
Nitrate (mg/L)	<1	n.d.	4	n.d.
TP (mg/L)	25–303	580–927	5	10

n.d.==not determined.
[a] References [159,160].
[b] Reference [161].
[c] Wastewater was settled in a primary settling tank.
[d] Reference [154].
[e] Reference [162].
[f] Example refers to laundry wastewater.

Table 5
Comparison of commercially available microalgae growth media in contrast to nutrient recovery cost from wastewater. Pricing as per described on the supplier's website.

Supplier	Products	Nutrient cost (€/L of culture)
NMCA[a]	f/2 medium kit, 50 L MKF250L	1.940
Sigma Aldrich[b]	50×, liquid, plant cell culture tested Prod. no. G0154	0.580
AusAqua Pty[c]	AlgaBoost (2000×) f/2	0.018
Varicon Aqua Solutions[d]	Concentrated liquid Cell-hi W	0.009
	Powder Cell-hi WP	0.0009
Pentair[e]	Proline f/2 algae feed Prod. no. 239800	0.0006
Wastewater[f]	@10 mg NH_4–N/L	0.001[g]
	@200 mg NH_4–N/L	0.00006[g]
	@500 mg NH_4–N/L	0.00003[g]

[a] Website: ncma.bigelow.org.
[b] Website: www.sigmaaldrich.com.
[c] Website: www.ausaqua.com.au.
[d] Website: www.variconaqua.com.
[e] Website: www.aquaticeco.com.
[f] Cost is based on 1€/m^3 as reported in our previous work [163].
[g] Assumes adequate availability of phosphorous and costs are calculated so that 0.082 mM of N are supplied to 1 L of culture.

Table 4
Comparative evaluation of the different technologies for the recovery of nutrients from wastewater.

Technology	Particle separation	Energy	Sterile	Selective extraction	Chemical addition
Membrane filtration	Simultaneous	Low-medium	Possible	Possible	No
Centrifugation	Simultaneous	High	Impossible	Impossible	No
Precipitation	Pre-treatment	Low	Possible	Impossible	Required
Stripping and Scrubbing	Pre-treatment	Very high	Possible	Possible	Required

growing microalgae. This margin provides scope for further processing such as autoclaving or further fractionation of the nutrients. Indeed, once waste-derived nutrients are recovered in solution, they become more amenable to further processing such as fractionation with membranes [163]. Nanofiltration membranes have been demonstrated to have a fundamental role in fractionating nutrients in aqueous solutions. Exploiting the differences in size and charge, NH_3–N and PO_4–P can be separated to a high degree using a NF270 (polyamide) membrane. This nanofiltration membrane retains over 90% of the PO_4–P and all the NH_3–N permeates through [164]. In addition, polyethersulphone membranes have been shown to reject up to nearly 70% of NH_3–N in solution [165]. Concentration of the recovered nutrient using RO can potentially reduce costs associated with pumping and transportation.

Aside from overall nutrient availability and sterility requirements, cultivation of microalgae from wastewater requires the appropriate ratio of nitrogen to phosphorous (molar N:P). A molar N:P ratio of 24.5:1 using standard f/2 growth medium is essential to ensure efficient microalgae growth and nutrient uptake [145,166]. Nevertheless, optimal N:P ratios for microalgae growth vary significantly among species due to strain varying metabolic pathways. More importantly, different N:P ratios and feed strategies lead to very distinct biochemical composition of the resulting biomass [34–36]. Cai et al. [153] have highlighted the different optimal N:P ratios for nutrient uptake from wastewater in relation to different microalgae species. Whilst *Chlorella vulgaris* was reported to have an ideal N:P ratio of 7, other species such as *Scenedesmus sp.* require an N:P ratio of approximately 30 to grow without nutrient limitation [153].

The composition of the wastewaters does not guarantee an optimal N:P ratio nor nutrient availability. Strategies which allow tailored growth media composition from wastewater are not sufficiently developed. Fig. 2 illustrates the proposed methodology for the recovery of growth media using membranes. The wastewater is first acidified so materials such as phosphorus and metals are solubilised. A 2-fold increase in soluble phosphorus and 2 to 9-fold increase in the availability of metals has been reported for dairy manure wastewater at pH 3 [163]. Prior to the membrane separation process, coarse particles must be screened through normal particle filtration. The maximum particle allowance is related to the fibre or tube diameter, or the spacer thickness in the case of spiral wound membranes. Microfiltration allows for the recovery of soluble materials in virtually sterile and particle-free solutions [51]. Nevertheless, in some cases where undesired complex organic compounds are present, ultrafiltration may be more appropriate [167–170]. Previous studies have reported on the separation by ultrafiltration of complex organic compounds such as pharmaceuticals and pesticides [170], humic and fulvic acid [171], volatile organic compounds (toluene and tetracloroethylene) [167], herbicide [168] and phenol and aniline [169].

The proposed methodology would allow the recovery and fractionation of nutrients from different wastewater sources. Depending on the nutrient availability, tailored microalgae growth media for optimal growth would be feasible adopting membrane technologies already available. Nonetheless, the filtration phenomena of nutrient recovery and fractionation are yet to be established. Fouling due to the presence of other materials such as polysaccharides and humic acids are expected to determine both rate of operation and maintenance [172,173]. Whilst the nutrient depleted wastewater may represent a less hazardous material to dispose of, the separate streams of nutrients could potentially have a large market value, for example in the fertiliser industry. Simultaneously, wastewaters may be more concentrated allowing for lower expedition costs such as pumping, transporting or further concentrating.

The utilisation of wastewater towards microalgae cultivation does carry some health and safety risks. Whilst the production of biofuels and energy from microalgae biomass benefits from the recycling of nutrients from wastewater with a lower impact of the health and safety considerations; microalgae-derived products for human consumption may not be realistically feasible. Therefore, the risks associated to algae cultivation from wastewater will very much depend on the product end use and on the source of the wastewater. The adequacy of a particular wastewater for microalgae cultivation is dependent upon the potential presence of pathogens, prions, toxic heavy metals and volatile organic carbons. Different types of wastewater will represent different health and safety risks due to their inherent nature. In this sense, animal derived wastewaters such as manure digestate and aquaculture may represent a lesser health and safety risk than those derived from municipal and industrial wastewater treatment plants.

3. Cell harvesting

Microalgae cell harvesting is perhaps the best documented application of membranes in the context of microalgae biorefineries. Nonetheless, herein membrane technology contends with other well established technologies such as centrifugation, sedimentation, coagulation–flocculation and dissolved air flotation [174,175]. Other less developed methodologies include ultrasound [176], electrodialysis [177] and ferric nanoparticles [178]. Amongst these, membrane dewatering of microalgae seems to be one the leading harvesting processes due to ease of scaling up, lower energy requirements and absence of chemical contaminants (Fig. 3). Moreover, whilst allowing

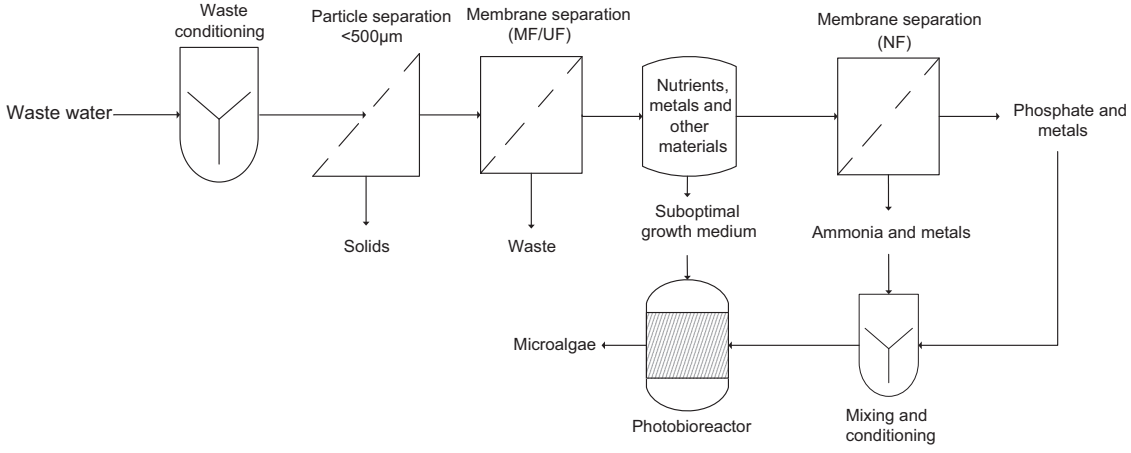

Fig. 2. Upstream of microalgae biorefinery concept - proposed methodology for the recovery of nutrients from wastewater as cell growth medium.

Fig. 3. Examples of membrane microfiltration systems for microalgae harvesting at Swansea University: (left) 200 L pilot-scale microfiltration unit fitted with a 0.1 μm PES spiral wound membrane (Koch), (right) 20 L bench top microfiltration unit fitted with a 0.2 μm PS fibre membrane (GE Healthcare).

for nearly 100% of cell recovery the recovery of media is suitable for reuse as a water conservation strategy. In contrast with other dewatering technologies such as centrifugation, membranes are limited by the maximum amount of solids permissible. Membranes can deal with suspensions up to around 10–15% solids which is ideal for the downstream processing of microalgae [9].

The characteristics of microalgae cells can be varied. Typically biomass concentration is below 0.1% solids, cell sizes range from 2–30 μm and cell's surface charge range between 5–40 mV (as measured by zeta-potential) [6]. The use of membrane filtration for microalgae harvesting has most commonly been reported across the microfiltration-ultrafiltration range. Nevertheless, applications of forward osmosis have also been reported. Table 6 summarises the applications of commercially available membranes which have been investigated for microalgae harvesting. Most of the membranes investigated refer to organic polymer-based membranes in various formats. This is probably due to their wide availability, high chemical compatibility, variety of designs and reasonable cost [50,179].

Throughout the literature the influence of the membrane pore size on the harvesting performance is ambiguous. On the harvesting of *Spirulina*, Rossi et al. [183] have tested several commercial membranes across the range 3 kDa to 1.5 μm pore size and different membrane materials. These authors showed that harvesting of *Spirulina* using membrane filtration was optimal across 40–100 kDa cut-off. Reportedly, a UF 40 kDa ceramic membrane showed the best performance and the authors argued that the membrane hydrophilicity and pore size led to less pore clogging and thus higher flux. Although *Spirulina* cell sizes are very large in comparison to other microalgae species, the optimal membrane pore size did not reflect that. In this particular case, the authors noted that shear stress induced by circulation had a noticeable effect on filament fragmentation: the filament size was reduced from several hundreds to around 10 μm. When comparing a 40 kDa ceramic membrane to a 0.4 μm PVDF membrane the authors reported an improvement of about 5 LMH (1 bar and crossflow velocity of 1 m/s) in relation to the 0.4 μm PVDF membrane. This was contrary to the much higher pure water flux for all MF membranes than that was obtained for the UF membranes. In conclusion, larger pore size did not translate into higher flux due to both pore clogging and adsorption of extracellular organic matter (EOM) causing irreversible fouling. Conversely, other authors have reported that due to the microalgae cell size range there is no benefit in using UF membranes in detriment of MF membranes. Bhave et al. [59] have discussed that on harvesting with UF or MF there was no benefit in using smaller pore size such as in UF membranes. Their argument was that given the microalgae's cell size, MF provides a very good separation at similar flux whilst operating at lower pressures than that needed for UF membranes [59]. The filtration of biological suspensions across the microfiltration pore size range is significantly affected by surface roughness and pore geometry [191]. Authors have reported that the influence of the membrane materials at around 0.1–0.2 μm pore size was not significant on the permeate flux during the filtration of biological suspensions. Nonetheless, at pore sizes of 0.45 μm MCE (mixed cellulose ester) membranes provided higher fluxes than PC (polycarbonate), PES (polyethersulfone) and CA (cellulose acetate). These results were attributed to morphological differences such as pore structure and roughness of the membrane [191]. Furthermore, according to some authors the maximum pore size is limited since, in the case of *Nannochloropsis sp.* with cell sizes ranging 3–4 μm, membranes with pore sizes > 0.5 μm produce slightly turbid permeates as some of the algal materials are not retained [59]. Contrary to this, recent work by Ahmad et al. [189] on harvesting of *Chlorella sp.* (3–5 μm cell size) reported a 1.2 μm cellulose triacetate (CTA) membrane with a stabilised flux of 100 L/(m^2 h) [189]. In addition, Rickman et al. [190] reported the use of a 5 μm MCE membrane for harvesting *Chlamydomonas* with an average cell diameter of 10 μm. In their work, the authors also found that very similar fouling rates occur for both MCE 50 kDa and 0.22 μm whilst no irreversible fouling was observed for the 5 μm membrane [190]. This tends to illustrate that there is a requirement for selecting membranes in relation to the microalgae cell sizes. In principle, larger microalgae species could be retained with looser membrane structures leading to higher flux rates. Nevertheless, higher permeate flux will also determine a higher rate of pore clogging due to increased particle flux towards the membrane's surface. Therefore, during continuous operation membrane efficiency is likely to quickly fall below of that observed for membranes with much smaller pore sizes. Less absorption of EOM and thus irreversible fouling may be observed using membranes with pore sizes close to that of the microalgae cell size being harvested, though leakage of cells could easily occur. In fact, for MF membranes the reported pore size is typically not a perfect measure of the actual pore size, as they filter via a depth filtration mechanism, and thus larger pores may allow cells larger than the nominal pore size to pass

Table 6
Harvesting of microalgae with different using commercially available membranes. n.d. – not determined, TFF – tangential flow flitration, DE – dead end filtration, FO – forward osmosis, CTA – cellulose triacetate, PAN – polyacrylonitrile, ATZ – alumina, titania and zirconia ceramic membrane, PVC – polyvinylchloride, PES – polyethersulphone, PVDF – polyvinylidene fluoride, PS – polysulphone, MCE – mixed cellulose esters, and CA – cellulose acetate.

Membrane					Microalgae species	Cost estimates (kWh/m^3)	Ref.
Pore size	Material	Mode	Scale	Flux[a] (LMH)			
FO	CTA	Flatsheet TFF	Lab	30 (23 bar[b], 0.22 m/s)	*Chlorella sorokiniana*	n.d.	[180]
FO (3–5 Å)	CTA	Bag FO	Lab	2 (n.d.)	*Chlorella vulgaris*	0.3	[181]
40 kDa	PAN	Flatsheet TFF	Lab	15–60 (0.5 bar, 0.5 m/s)	*Haslea ostrearia* and *Skeletonema costatum*	n.d.	[182]
40 kDa	PAN	Flatsheet TFF	Lab	15 (1 bar, 1 m/s)	*Arthrospira platensis (Spirulina)*	n.d.	[183]
50 kDa	ATZ	Tubular TFF	Lab	80 (1 bar, 3 m/s)	*Arthrospira platensis (Spirulina)*	n.d.	[58]
50 kDa	PVC	Hollow fibre TFF	Lab	46 (0.35 bar, 0.17 m/s)	*Scenedesmus quadricauda*	n.d.	[184]
0.1 μm	PES	Spiral wound TFF	Pilot	40 (1.95 bar, 1.01 m/s)	*Scenedemus sp.*	0.9–2.23	[185]
0.1 μm and 0.2 μm	PVDF (hydrophilic) and ceramic	Hollow fibre and tubular TFF	Lab	30–100 (1–2 bar, 0.28–4 m/s)	*Nannochloropsis sp.*	0.7	[59]
0.2 μm	PS	Hollow fibre Submerged	Lab	29[c] (0.3 bar, 625 L air/(h m^2))	*Heterocapsa triquetra*	n.d.	[186]
0.22 μm	PVDF (hydrophilic)	Cassette TFF	Lab	20 (2 bar, n.d.)	*Tetraselmis suecica*	2.1	[174]
0.22 μm	PVDF (hydrophilic) and MCE	Flatsheet TFF	Lab	284–350[c] (0.4–0.6 bar, 0.43–0.84 m/s)	*Chlorella sp.*	n.d.	[187]
0.45 μm	PVDF (hydrophilic)	Cassette TFF	Lab	n.d. [c]	(Several)	n.d.	[188]
1.2 μm	CA	Flatsheet TFF	Lab	100 (1 bar, 0.13 m/s)	*Chlorella sp.*	n.d.	[189]
5 μm	MCE	Stirred cell	Lab	22 (1 bar, 0.82 m/s)	*Chlamydomonas*	n.d.	[190]

[a] Stabilised flux given at specific TMP and cross flow velocities.
[b] Osmotic pressure difference.
[c] Water treatment where microalgae concentrations are very low (below 0.002% dry mass).

through. Smaller pore size membranes, in the range of 10- to 100-fold smaller than the microalgae being harvested, may lead to less pore clogging due to steric effects, however specific absorption phenomena of EOM on the membrane surface is likely to increase. Depending on the microalgae cell's size and membrane pore size, membrane fouling may be caused by whole cell, EOM or both.

The suitability of microfiltration for dewatering microalgae has previously been discussed and the mechanisms of fouling have been thoroughly analysed. Babel and Takizawa [192] showed that for dewatering of *Chlorella*, membrane fouling was highly dependent on the amount of extracellular organic matter (EOM) and that cake resistance was independent from the membrane material [192]. Other researchers have observed that even though higher cross flow velocities could minimise fouling to a certain extent, this also caused increased leaching of EOM due to increased shear. They have also noted that membrane fouling is directly related to operating ΔP, however overall membrane performance is dependent on the properties of the microalgae culture such as age, shape and debris [182,193,194]. In fact, since microalgae can excrete 6×10^{-8} μg/cell day of extracellular organic carbon, older cultures will consequently represent a more difficult filtration [195]. Moreover, different cultivation strategies which lead to different biochemical compositions may also determine the rate of filtration.

Only recently, membrane modification aimed at reducing fouling formation has been reported. Cross-linking 1–3% ponivinyl alcohol (PVA) to a 4 μm polyethylene terephathalate (PET) membrane seemed to retard fouling and somewhat improve overall membrane flux [196]. Other developments include in-situ manufacture of 0.013–0.036 μm PVDF membranes for the submerged filtration of microalgae. Although the highly porous PVDF membranes allowed stabilised fluxes around 17–42 LMH, the application of such technology is very limited and only feasible for biomass concentrations up to 0.35% solids. In this work an energy consumption of 0.77–0.91 kWh/m^3 was reported [197,198].

Very few cost estimates related to harvesting microalgae using membrane filtration can be found in the literature. Mohn [199] reported power consumption for five different vacuum filter units to be 0.1–5.9 kWh/m^3. However, these technologies do not represent the current processing requirements for microalgae dewatering since new technologies have become available and there is currently focus on different algal species [199]. Much of the research into microalgae harvesting has been performed with lab-scale apparatuses featuring lab-grade equipment such as peristaltic pumps. As a result, the energy consumption estimates do not conform to that of a pilot or full scale membrane filtration system. Furthermore, authors do not specify the specific methodologies for measuring energy consumption. Therefore, appropriate methodologies for determining energy requirements during continuous operation are yet to be developed. Only recently, pilot-scale harvesting of microalgae by microfiltration has been reported. In this study, the cost of harvesting *Scenedesmus sp.* was determined as 2.23 kWh/m^3, nevertheless a modelling approach identified a potential cost reduction down to 0.90 kWh/m^3 depending on the initial biomass concentration and membrane area [185].

There are inherent limitations to membrane filtration technology. Fouling due to EOM is a major issue which significantly reduces the rate of filtration. Surface modification of membranes which minimise the adsorption of EOM is yet to be established. Whilst membranes allow the concentration of microalgae up to 15% solids, other technologies may be better suited for further biomass concentration. It is expected that synergetic approaches using membrane technology coupled to other technologies will become an option is some circumstances. Synergetic approaches using membrane technology and centrifugation may represent a strategy where both CAPEX and OPEX are minimised. In this approach membranes could be used as a pre-concentrating step for biomass 5–10% solids, whilst centrifugation would allow to a final dewatered product with 10–25% solids. Finally, some microalgae species such as flagellated microalgae are shear sensitive and thus for some specific applications membrane filtration may not be ideal.

Membrane filtration poses itself as a leading microalgae dewatering technology however, there is no conformity in the literature. The variety of membranes available which may be operated at different settings of pressure, cross-flow velocity, concentration and temperature associated with the diversity of microalgae species under different physiological states, highlights the fact that every microalgae species represents a unique challenge. There might not be a specific answer for the general harvesting of microalgae but instead each unique species will require a unique set of operating considerations.

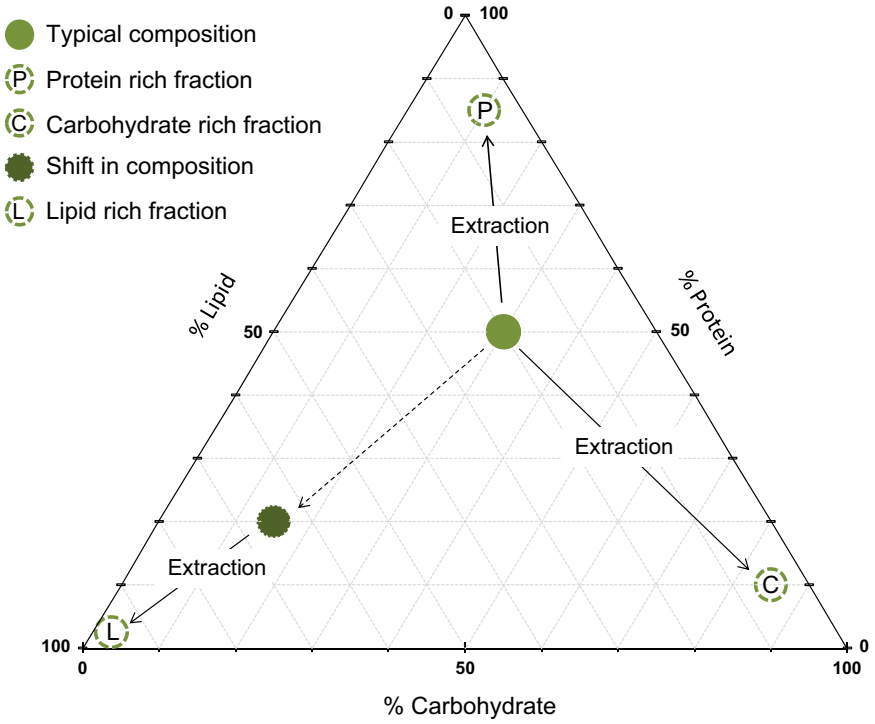

Fig. 4. Triangular plotting of the biochemical compositions for the different microalgae fractions obtained by DSP strategies. Target products are proteins and carbohydrates by membrane filtration and lipids by extractive methodologies such as solvent or supercritical CO_2.

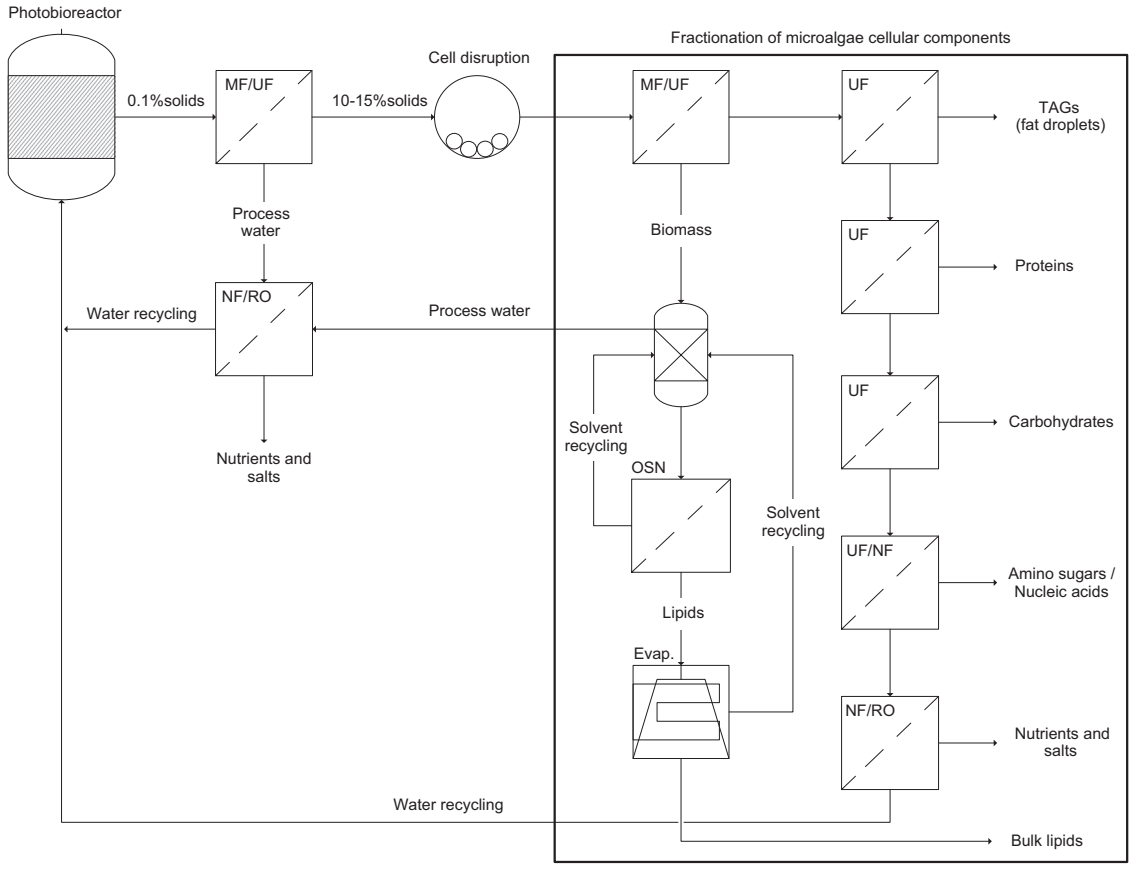

Fig. 5. Proposed methodology for the integration of membrane filtration in downstream processing of microalgae. It assumes that TAGs are possible to extract ahead of proteins however, bulk part of the lipids will remain with the biomass. These separations would be based on physico-chemical properties and benefit from diafiltration strategies to increase purity of the product.

4. Downstream processing (DSP) of microalgae

In this section we will review the documented technologies associated to the extraction of microalgae cellular components in a biorefinery context. Moreover, we will assess the feasibility of membrane technology in such context and identify the potential for further developments which enable the microalgae biorefinery approach.

The biochemical composition of microalgae may be simplistically divided into proteins, lipids and carbohydrates with traces of metals and pigments. The difficulty of DSP of microalgae cellular metabolites tends to be related to the accessibility to these materials. Much of the lipid fraction may be part of the cellular structure such as PUFA's and phospholipids in the cell's membrane which are relatively inaccessible [200]. In contrast, under certain environmental or stress conditions additional neutral lipids in the form of triacylglycerides (TAG's) are formed [201]. Once the cell's membrane is disrupted, these storage lipids (TAG's) are more easily accessible and may be separated using mild techniques [200]. In addition cell wall carbohydrates may account for as much as 54% of the cell wall structure [202]. Pigments are also typically present in the cell's membrane and difficult to extract without using harsh solvents [203].

Paramount to the DSP strategy is the disruption of the biomass to facilitate access to the intracellular products. The available options, advantages and disadvantages have been previously reviewed by several authors [204,205]. The essential requirements for cell disruption are efficiency of disruption, relatively low energy inputs and product preservation. The nature of the disruption process can affect the colloidal structure and thus limiting the fractionation of algal cellular components based on membrane filtration.

Within the biotechnology sector, although akin to yeast and bacteria, microalgae pose themselves as a completely new set of challenges owing to the tough cell wall and multiple viable products. Most the DSPs of microalgae materials rely on typically harsh conditions, energy intensive or on chemical additions which ultimately contaminate and devalue the biomass. The isolation of algal soluble proteins was reportedly achieved via ion exchange chromatography. The final product obtained had 64% proteins and 24% carbohydrates with 100% solubility at pH above 5.5 and excellent emulsifying properties, useful in food applications requiring protein additions [19,23]. More recently, other authors have used HCl (2 M) and NaOH (2 M) to extract proteins from undisrupted microalgae biomass. Using isopropanol as a defatting strategy prior to protein extraction, 30% protein extraction yields were achieved [206]. Other methodologies for protein recovery such as flash hydrolysis have also been reported. Subcritical water at 200–350 °C allowed for 30–66% protein extraction (based on nitrogen). This methodology also allowed recovering lipid-rich intermediates collected after flash hydrolysis [207]. In their review Vanthoor-Koopmans et al. have highlighted the use of ionic liquids and surfactants for the selective separation of lipids and proteins, respectively [10]. Solvents and supercritical CO_2 have been widely reported as suitable strategies for the recovery of algal oils and pigments. Reportedly, over 90% of TAGs may be recovered by supercritical CO_2 whereas solvent-based processes such as hexane, chloroform, dimethyl ether and methanol yield $<40\%$ lipids recovered [208–212].

Even though these methodologies are deemed suitable for the targeted product, they are typically harsh, energy intensive and obliterate the remaining microalgae products. Examples of the application of membranes for the DSP of microalgae metabolites are very few. Only recently the purification of TAG via membrane filtration has been reported with encouraging results. Giorno et al. [213] have shown that in a double step using both 100 kDa and 30 kDa regenerated cellulose (RC) membranes, microalgae metabolites such as proteins, sugars and TAG's could be extracted from the disrupted biomass. The 30 kDa RC membrane showed rejection factors of 0.89 for protein and 0.36 for glucose. Overall recovery was low with rejection factors for TAG ranging 0.16–0.23. Moreover, the final TAG solutions still contained both sugars and proteins [213]. Although this may not hinder the conversion into biodiesel, TAG's were not effectively separated from proteins and carbohydrates.

There is an obvious lack of methodologies which enable the extraction of multiple algal products whilst preserving their properties. Product separation based on chemical-free, low energy and mild operating conditions is potentially possible through membrane filtration. Nevertheless, the integration of membrane technology in such a context is far from being developed. Ideal membrane processing of microalgae metabolites would enable the extraction of protein-rich and carbohydrate-rich fractions, leaving the bulk of the lipids with the remaining biomass. TAGs may be extracted via membrane separation [213], however this type of lipid only accounts for a proportion of all lipids [201]. UF membranes in the region of 1–100 kDa may play a fundamental role in the fractionation of such microalgae metabolites. Fig. 4 illustrates such a proposition, with proteins and carbohydrates being separated via membrane technology based on size and charge exclusion. The bulk of the lipids would stay trapped in the biomass this would generate a significant shift in the biochemical composition. The lipid-rich biomass could potentially undergo appropriate lipid extraction for maximum yields and product purity similar to that obtained with supercritical CO_2. Other potential applications of such lipid-rich biomass would suit direct transesterification into biodiesel [214,215] or thermo-chemical conversions such as hydrothermal liquefaction [216,217].

Organic solvent extraction of algal-lipids is perhaps the most widely used extraction method. The recovery of both lipids and solvents becomes costly and environmentally unfriendly. Although not definitely established, organic solvent nanofiltration (OSN) may also have a role in this process. Recent developments have shown the recovery of hexane from soybean edible oil is feasible using commercially available membranes. With OSN, oil recovery yield was reported to be 70–80% from oil-solvent mixtures ranging 10–35% w/w [218,219]. OSN could potentially allow the recovery of the lipid extracts at the same time as recovering the organic solvent. This would minimise costs with evaporation and solvent

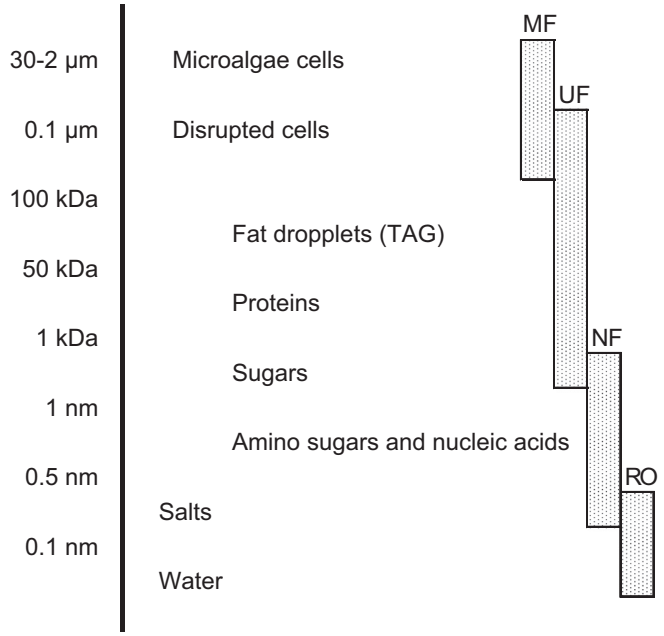

Fig. 6. Membrane fractionation of microalgae components in relation to size and membrane process. MF – microfiltration, UF – ultrafiltration, NF – nanofiltration, RO – reverse osmosis. Adapted from [67].

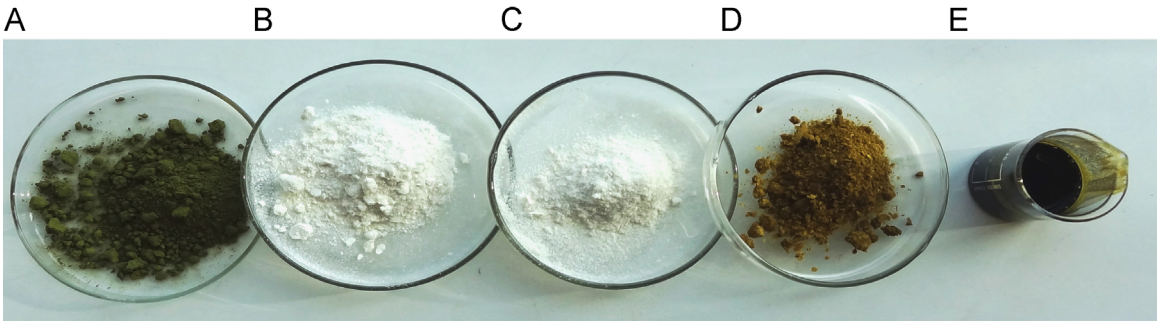

Fig. 7. Microalgae products resulting from membrane-based DSP systems: (A) feed (algae powder), (B) proteins, (C) carbohydrates (D) lipid rich biomass and (E) lipids (by solvent extraction).

requirement. The integration of OSN in the DSP of microalgae is demonstrated in Fig. 5.

The proposed strategy for the DSP of microalgae illustrates the application range of membrane technology in relation to the process requirements and targeted products. The proposed relation of the membrane pore size to the targeted product is demonstrated in Fig. 4. It is assumed that storage lipids (TAG's) are possible to extract via MF-UF prior to protein extraction. The feasibility of such sequence of extraction is expected to be highly dependent on the physical-chemical properties of each component. Parallels can be drawn from the membrane fractionation of milk in the dairy industry. Pilot-scale MF, UF and NF membrane processes were designed and evaluated for fractionating casein micelles from milk serum proteins [220], lactose [221] and minerals [221,222]from milk. These processes have been thoroughly reviewed by several authors. Exploiting the size difference of the components in milk, the use of membranes across the range MF to RO allows separating fat globules, casein micelles, serum proteins, lactose, salt and minerals and water [67,223].

Fig. 6 illustrates such application of membrane separations for a different range of microalgae products based on soluble materials. Whole and disrupted microalgae cells may be separated across the MF range whereas the fractionation of the algal materials is likely to take place across the UF-NF range. Whilst this strategy proved to be successful in the dairy industry, membrane fractionation of microalgae products is still very much in its infancy.

5. Future prospects

With new worldwide research calls on biorefineries for multi-products from microalgae, the research on algae-based products and associated methodologies is set to expand frantically. The prospects of a microalgae-based economy are still bleak due to its reliance on the extraction of oils for biodiesel. Most importantly, the associated technologies do not seem to address the real needs of a biorefinery approach. The main drive for the success of a microalgae biorefinery-based approach is costs and product market. Recent developments in the processing and formulation of nutrients from wastewater seem to reduce costs and energy associated to growth medium. Nevertheless, further developments in the fractionation of nutrients aimed at optimal growth medium are required. Dewatering of microalgae cultures is still seen as a significant cost. Whilst much has been published on membrane dewatering of microalgae, the influence of pore size, membrane material and costs is not clear. Only a handful of cost estimates can be found in the literature and typically these are associated to lab-scale apparatuses. As the research into the application of membranes for dewatering microalgae continues membrane surface modification, pilot-scale units and effective estimation of costs are expected to emerge in the literature.

Bridging the success observed in the dairy industry, membrane fractionation of microalgae products seems to be front runners in the race to realise the potential of a microalgae-based economy. Focus on the primary fractionation of microalgae products is currently needed. Due to their typical size and nature, proteins and carbohydrates are natural candidates for membrane-based separations. Once these two products are separated from the disrupted biomass, the extraction of structural lipids may take place. OSN may also have a potential application in the extraction of lipids via solvent extraction. Fig. 7 illustrates what soon could be a reality.

6. Conclusions

Membrane filtration technology has come a long way and is still expanding rapidly. The application of membranes into biorefineries is novel and lacking in both materials and methods. This work has discussed the latest developments, limitations and future directions of membranes in microalgae biorefineries. The future of microalgae as a feedstock for sustainable biofuel is still uncertain. Low-cost methodologies which maximise product output are vital for this novel technology. The proposed integration of membrane technology for both upstream and downstream requirements is based on previously established applications. It is expected that as the research community attempts to realise the potential of such feedstock, membrane technology has a fundamental role in this process. Nonetheless, only a combined effort between the engineers, biologists and other technologists will bring this to reality.

Acknowledgements

This work was developed for the EnAlgae project, which has received European Regional Development Funding via the INTERREG IVB NWE programme and support from the Welsh Government's Targeted Match Fund.

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